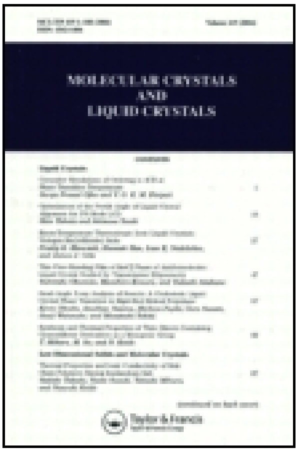


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Polarons and Bipolarons in Sigma-Conjugated Polymer Backbones

S. Jeyadev [a] , S. R. Phillpot [a] & M. J. Rice [a]
[a] Xerox Webster Research Center, 800 Phillips Road 0114-38D, Webster, NY, 14580

Version of record first published: 28 Mar 2007.

To cite this article: S. Jeyadev , S. R. Phillpot & M. J. Rice (1988): Polarons and Bipolarons in Sigma-Conjugated Polymer Backbones, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 160:1, 433-442

To link to this article: http://dx.doi.org/10.1080/15421408808083037

Mol. Cryst. Liq. Cryst., 1988, Vol. 160, pp. 433–442
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Polarons and Bipolarons in Sigma-Conjugated Polymer Backbones†

S. JEYADEV, S. R. PHILLPOT AND M. J. RICE

Xerox Webster Research Center, 800 Phillips Road 0114-38D, Webster, NY 14580

A coupled electron–lattice model of a saturated homopolymer, such as a poly(organosilylene), is introduced. It shows that the states available in the polymer backbone for the addition or excitation of electrons, or holes, are localized intragap states that are spontaneously generated by bond order polaron formation.

I. INTRODUCTION

One-electron theory models[1] that stress electron–lattice coupling have been successful in interpreting the observed solid state properties of conjugated polymers such as polyacetylene.[2] In this paper we report on the extension[3] of this type of model to describe a *saturated* polymer. Specifically, we have constructed a microscopic model of the backbone states of a tetrahedrally bonded polymer with formula $-(-AR_2-)_n-$, where A denotes a Group IVA atom and R an organic side group. This type of saturated homopolymer includes the polysilylenes[4] and the polygermylenes[5] as well as, of course, the wide class of carbon based polymers. They have band gaps in the ultaviolet (UV).

Very interestingly, the model shows that, provided the electron–lattice interaction is not so strong that scission of the polymer occurs, the saturated polymer can support polaron states with localized gap-state and infrared (IR) vibrational characteristics similar to those found in models of conjugated polymers with non-degenerated ground states.[6,7] In particular, there is a paramagnetic *polaron*, a diamagnetic *bipolaron*, and a charge-neutral polaron *excitation* that is the relaxed photoexcitation of the polymer. They involve localized regions of

---

†Research supported in part by the National Science Foundation—Solid State Chemistry—Grant DMR-8416511.

reduced *bond order* and, hence, of weakened bonds. For the UV-sensitive *polyorganosilylenes*[4,8] we estimate that the width of the neutral polaron is only a few bond lengths, thus providing a specific mechanism for energy localization.

II. THE MODEL

The microscopic model is defined by the Hamiltonian

$$H = 2\Delta_0 N + \sum_j \left(Br_j^{-l} + \tfrac{1}{2}\mathrm{M}\mathbf{R}_j^2\right) - \Delta \sum_{j,\sigma} \left(a^+{}_{j,\sigma} b_{j,\sigma} + h.c.\right) - \sum_{j,\sigma} V_{j,j-1}\left(a^+{}_{j,\sigma} b_{j-1,\sigma} + h.c.\right) \qquad (1)$$

It describes N(N → ∞) A atoms of mass M whose instantaneous positions and velocities in a *trans* chain backbone (lying along the x-axis) are denoted by $\mathbf{R}_j$ and $\dot{\mathbf{R}}_j$, respectively ($j = 1,2,$—N). It is assumed that the electronic states of the backbone are derived from interaction of atomic-A sp^3-like orbitals, $\Psi_a\,(\mathbf{x} - \mathbf{R}_j)$ and $\Psi_b(\mathbf{x} - \mathbf{R}_{j-1})$, which point along the same A—A bond (see Figure 1). The other atomic hybrid orbitals, pointing along the A—R bonds, are supposed to be *effectively* decoupled from the *a* and *b* orbitals on account of strong bonding with the side groups R. The matrix element describing the interaction of the *a* and *b* orbitals is denoted by $V_{j,j-1}$ and taken to have the specific form[9,10] $V_{j,j-1} = Dr_j^{-2}$, where D is a constant and $r_j \equiv |\mathbf{R}_j - \mathbf{R}_{j-1}|$. At the same time, a repulsive interaction $U_j = Br_j^{-l}$ is assumed to exist between the same pair of atoms, j and $j - 1$, where B and l are constants. Together, $V_{j,j-1}$ and U_j microscopically define the electron lattice interaction. $a^+_{j,\sigma}$ and $b^+_{j,\alpha}$ are fermion operators which create, respectively, an electron with spin σ in the a and b orbital of the atom j. Δ denotes the matrix element

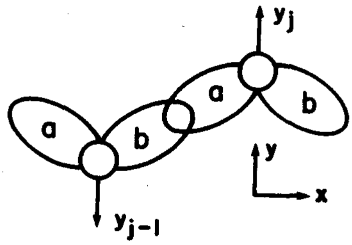


FIGURE 1 The *trans* polymer model.

between a and b orbitals on the same atomic site and $4\Delta_0$ denotes the atomic sp^3 promotion energy. The energies in (1) are measured relative to the atomic energies and there is one electron per orbital.

The ground state of (1) is that of a covalent semiconductor[11] with bonds of equal length r and an electron energy spectrum, ϵ_κ, given by

$$\epsilon_\kappa - \Delta_0 = \pm\,[V^2(r) + \Delta^2 + 2V(r)\,\Delta\cos(\kappa\, a)]^{1/2} \equiv \pm\, E_\kappa \qquad (2)$$

Here, $V(r) = D/r^2$, $2a = 2r\sin\theta$ is the period of the *trans* chain, 2θ is the tetrahedral bond angle and the allowed wavevectors, κ, are defined in the extended zone $-\pi < \kappa\, a \leq \pi$. The covalent energy gap, E_g, is just $2\,(V(r) - \Delta) \equiv 2\,a$. If $\Delta = 0$, the polymer consists of $N - 1$ independent bonds in which the electronic energy levels are at $\Delta_0 \pm V(r)$. If $\Delta \neq 0$, the bonds become coupled and charged delocalizes from them toward the atomic sites. Minimization of the total energy per bond $E(r)$ with respect to r fixes the equilibrium bond length r_0 according to

$$B/r_0^l = [4\,V/l(N - 1)] \sum_\kappa (W_\kappa/E_\kappa) \qquad (3a)$$

and leads to the result

$$E_b = 2\Delta_0 - [2/(N - 1)] \sum_\kappa E_\kappa[1 - (2VW_\kappa/l)E_\kappa^{-2}] \qquad (3b)$$

for the binding energy (BE) per bond, $E_b = E(r_0)$, where $W_\kappa = V + \Delta\cos(\kappa\, a)$ and $V \equiv V(r_0)$. Similarly, $K(r) = \partial^2 E/\partial r^2$ may be evaluated to give

$$\kappa = [2(l-2)\beta/3(N-1)]\sum_\kappa W_\kappa E_\kappa^{-1} - [2\gamma^2/(N-1)]\sum_\kappa \Delta_\kappa^2 E_\kappa^{-3}, \qquad (4)$$

the bond stretch force constant, $K = K(r_0)$, where $\Delta_\kappa = \Delta\sin(\kappa a)$, and $-\gamma$ and β are, respectively, the first and second derivatives of $V(r)$ evaluated at r_0. The frequency of the transverse optical (TO) phonon of the polymer is $\omega_{TO} = (4K/M)^{1/2}\cos\theta$. The sums in (3a), (3b) and (4) are easily evaluated in terms of elliptic functions. Together with the formula for E_g they may be used, in principle, to determine the four microscopic parameters B, l, D and Δ from the experimentally observed values of r_0, E_b, K and E_g.

III. POLARON AND BIPOLARON SOLUTIONS

We now consider the states available in the polymer for the addition or excitation of electrons or holes. Because of the nature of the ground state we anticipate polaron formation that involves bond length relaxation. If we require the latter to leave the length of the polymer unchanged we are led to consider a static displacement pattern of the form of a TO phonon, i.e., $y_j = (-1)^j (u_j/2 \cos\theta)$, where y_j denotes the displacement in the y direction of the jth atom from its ground state equilibrium position $\mathbf{R}_j^0$ (see Figure 1). If the bond relaxation (elongation) amplitude u_j is sufficiently small and only slowly varying over interatomic distances we may expand (1) about $\{\mathbf{R}_j^0\}$ and express the orbital amplitudes for electronic states with levels ϵ_n close to the gap edges as $a_{j,n} = (-1)^j A_n(x)$ and $b_{n,j} = -(1)^j B_n(x)$, where x denotes an arbitrary point along the polymer axis in a continuum description, $ja \rightarrow x$. The electronic states and $u_j = u(x)$ are then found to be determined by the simultaneous solution of

$$\epsilon_n A_n(x) = Q_-(x) B_n(x) \tag{5a}$$

$$\epsilon_n B_n(x) = Q_+(x) A_n(x) \tag{5b}$$

$$\gamma u(x) \equiv v(x) = -(2\gamma^2/K_0)\textstyle\sum_n [p_n(x) - p_n(\infty)]\nu_n, \tag{5c}$$

where the operators Q ± (x) and the local *bond orders* $p_n(x)$ are defined by

$$Q_\pm(x) = -a - (a^2/2)V\nabla_x^2 + v(x) \pm V\,a\,\nabla_x \tag{6a}$$

$$p_n(x) = [A_n^*(x)B_n(x) + c.c.]/2. \tag{6b}$$

$v(x)$ in (5c) is the potential felt by the electrons due to the lattice distortion described by $u(x)$, ν_n is the electronic occupation of the nth level and K_0 is the unscreened force constant given by the first term of (4). A_n and B_n are normalized according to

$$\int (dx/a)[|A_n(x)|^2 + |B_n(x)|^2] = 1 \tag{7}$$

and the total energy of the polymer is

$$E = \sum_n \nu_n \epsilon_n + (K_0/2)\int (dx/a)u(x)^2 \tag{8}$$

where in (7) and (8) the integral extends over $L = N/a \to \infty$, and the levels ϵ_n are measured relative to Δ_0.

We have derived polaron solutions of (5) which have the form $u(x) = \epsilon^2(\alpha\gamma)\,\mathrm{sech}^2(x/\xi_p)$, where $\epsilon = (\Delta V)^{1/2}(a/\xi_p)$, and are accurate to order $(a/\xi_p)^2\,(V/2\alpha)^2 \equiv \lambda^2$. The corresponding spectrum of electronic states consists of

(a) a pair of localized *intragap* levels with energies $\pm\,(\alpha^2 - \epsilon^2)^{1/2} \equiv \pm\,\epsilon_p$, and wavefunctions $A_\pm(x)\,f_0(x + x_0)$ *and* $B_\pm(x) = \mp\,f_0(x - x_0)$, where $f_0(x) = (a/4\,\xi_p)^{1/2}\,\mathrm{sech}(x/\xi_p)$ and $x_0 = (V/2\alpha)a$. The polaron halfwidth, ξ_p, is

$$\xi_p = \xi_p(\nu) = (2K_0\Delta V/\alpha\gamma^2)(\alpha/\nu). \tag{9}$$

In (9) we have introduced $\nu = \nu_+ + 2 - \nu_-$, where ν_+ and ν_- are the electronic occupations of the upper and lower intragap levels, respectively. Note that ϵ is proportional to ν.

(b) conduction (+) and valence (−) band states with energies $\epsilon_\pm\,(k) = \pm\,(\alpha^2 + \Delta V(ka)^2)^{1/2}(k \neq 0)$, and wavefunctions $A_{\pm,\,k}(x) = f_k(x + x_0)$, $B_{\pm,\,k}(x) = \mp\,f_k(x - x_0)$, where,

$$f_k(x) = (a/2L_k)^{1/2}\exp(-ik\,x)[k\xi_p + i\,\tanh(x/\xi_p)], \tag{10}$$

and $L_k = L(1 + (k\,\xi_p)^2) + 2\xi_p$. The wavevectors k are obtained from $kL = 2\pi\,\tau + \theta_k$, where $\tau = 0, \pm1, \pm2, \ldots$, and $\theta_k = 2\tan^{-1}(1/k\xi_p)$ is the phase shift experienced by the band states in their transmission through the region of the polaron.

IV. DISCUSSION AND CONCLUSIONS

We first note that the quantity $\lambda = \nu(\gamma^2/4K_0\Delta) \sim \nu(V/4\Delta(l - 2))$ is a measure of the strength of the electron–lattice interaction. Formally, if $\lambda \to (V/4\Delta)^{1/2} < 1$, $\epsilon_p \to 0$, the energy of an unpaired orbital. This suggests that if $\lambda \simeq 1$, the addition or excitation of an electron or hole will cause *scission* of the polymer.

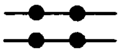
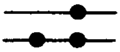
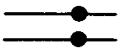
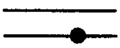
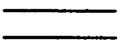
The presence of the polaron removes precisely one state per spin from the occupied valence band. Consequently, (and as may be directly verified from Eq. (10) there is a valence band *charge deficit* in the region that is equal to the charge of two electrons.[1] The total charge, Q, of the polaron is thus found to be $Q = e(\nu_+ + \nu_- - 2)$, where e denotes the charge on an electron. Since either intragap level may accommodate, 0, 1 or 2 electrons, it follows that there is a paramagnetic polaron ($\nu = 1$) with charge ± e, a spinless *bipolaron* ($\nu = 2$) with charge ± $2e$ and a *charge-neutral* polaron ($\nu = 2$). The occupancies of the intragap levels, the spin states and the stable excited ($\nu = 3,4$) states of these polarons are depicted in Table I. The neutral polaron corresponds to a relaxed electron-hole pair *excitation* and may be photogenerated in the polymer. Free charges are not, therefore, directly created by photoexcitation. In calculating the polaron formation energy, $E_p\ (\nu)$, from (8) we find that the (downward) shifts of the valence band states $\epsilon_-(k)$ relative to their ground state values (due to the phase shift θ_k) sum *precisely* to ϵ_p per spin. Thus, remarkably, there is an exact cancellation of the energy of the lower intragap level $-\epsilon_p$. In consequence $E_p(\nu)$ is just

$$E_p(\nu) = (\nu/3\alpha)\epsilon^2\,(\nu) + \nu(\alpha^2 - \epsilon^2(\nu))^{1/2}, \tag{11}$$

from which the polaron BE, $\epsilon_B\ (\nu) \simeq -\nu\,\epsilon^2(\nu)/6\alpha$, is seen to vary as ν^3. There is, therefore a strong tendency for two polarons on the same chain to form a bipolaron.

TABLE I

Characteristics of the Polaron States of the Saturated Homopolymer

charge	gap-state occupancy*	spin states	stable excited state
2e		S = 0	
e		S = ½	
0		S = 0,1	
-e		S = ½	
-2e		S = 0	

* *Each solid circle denotes an electron. The gap states are "screened" by a valence band charge deficit of 2 electrons*

An *approximate* calculation of the vibrational modes of the polarons may be carried out by introducing bonding and antibonding states, $\sqrt{2}\,\Psi_n^{\pm}(x) = A_n(x) \pm B_n(x)$ for the electrons and then, in considering their response to small oscillations about the static polaron solutions, neglecting the coupling between Ψ_n^+ and Ψ_n^-. The problem may then be mapped on to the corresponding problem for the Holstein *large* polaron[12] with the result that the frequencies, Ω_s, of the odd parity infrared modes are

$$\Omega^2 s = \omega^2_{\mathrm{TO}} s(s + 5)/(s^2 + 5s + 4) \qquad (12)$$

where $s = 0,2,4,\ldots$. This spectrum consists of a zero-frequency translational model ($s = 0$) and a quasi-band of localized modes beginning at 0.88 ω_{TO} and extending up to just below ω_{TO}. It implies a quantum correction to $E_p(\nu)$ of order-$\hbar\omega_{\mathrm{TO}}/2$. If we denote by m the mass of an electron, the adiabatic translational masses of the polarons are

$$m_p(\nu) = |Q|(m/e) + (4\epsilon^5(\nu)M)/[15(\alpha\ \gamma\ \alpha)^2(\Delta V)^{1/2}] \qquad (13)$$

where the second term has been obtained by boosting the static polaron solution and calculating the resulting kinetic energy of the lattice from (1).

For the poly-organosilylenes the observed energy, $E_g(N)$, of maximum UV absorption (~4 eV for $N \rightarrow \infty$) exhibits a striking dependence on polymer length, aN.[13,8] This is consistent with the electronic transitions occurring between delocalized bonding and antibonding states of the Si backbone.[14] For *finite* N, (2) leads to the result $E_g(N) = 2[\alpha^2 + 2V\,\Delta\,(1 - \cos(\pi/N))]^{1/2}$ for the energy gap, and is able to account for the N-dependence observed[13] for poly(dimethylsilylene) for $N = 3$ to 24 if $V = 3.3$ eV and $\Delta = 1.3$ eV. Further, with the experimental values[15] $r_0 = 2.34$ Å and $K \simeq 9.5$ eV Å^{-2}, we obtain $\gamma = 2V/r_0 = 2.8$ eVÅ^{-1} and, from (4), $K_0 \simeq 9.9$ eVÅ^{-2}. These values lead to the estimates of ξ_p/a, $u(o)/r_0$,

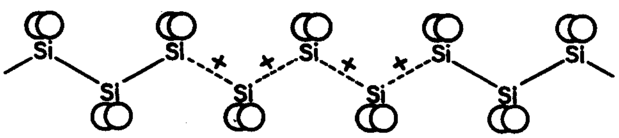


FIGURE 2 The hole bond-order polaron in a polysilylene polymer. The broken lines depict weakened bonds.

ϵ_B, m_p/m and $\Delta\epsilon_s = 2(\alpha - \epsilon_p)$ that are presented in Table II. In calculating the m_p from (12) M was taken to be the mass of the silicon atom and the two methyl side groups. It is seen that the polaron ($\xi_p \sim 5a$) is estimated to be weakly bound. For adiabatic motion, i.e., for temperatures $T << \sim m_p v_0^2/2k_B \sim 600K$, where $v_0 = 4\xi_p \omega_{TO}$, it would behave like a free electron or hole. This is consistent with the observations that the polysilylenes support hole transport.[16,17] On the other hand, the narrow width $\xi_p \sim 2.5a$ found for either the bipolaron or neutral polaron suggests that formation of the latter excitation would be a very effective mechanism for energy localization and may well be the precursor of polymer scission. The estimate $\Delta\epsilon_s \simeq 0.32$ eV for the corresponding Stokes shift is in agreement with the values observed[18] for the UV-sensitive(alkyl) poly-organosilylenes. Numerical minimization of the energy of the discrete model (1) with a $\text{sech}^2\,[(j - j_0)\,(a/\xi_p)]$ ansatz for u_j, and with B and l determined[19] from (3a) and (4), confirms the results of Table II for the polaron but indicates a significantly narrower width, $\xi_p \sim 1.65a$, for the neutral polaron. (Narrower widths for the charged polarons also can be expected if the electronic polarizability of the polymer medium is taken into account).

Photoinduced absorption measurements on the poly-organosilylenes should be able to detect the intragap levels of the neutral polaron. While photoexcitation of a single chain does not create free charges, *interchain* photoexcitation in the presence of an electric field would lead to the generation of free polarons on different chains and,

TABLE II

Polaron parameters for poly(dimethylsilylene)

	$\nu = 1$	$\nu = 2$
ξ_p/a	5.3	2.6
$u(0)/r_0$	1.0×10^{-2}	4.1×10^{-2}
$-\epsilon_B$(eV)	1.3×10^{-2}	0.10
m_p/m	1.7	24
$\Delta\epsilon_s$(eV)	7.8×10^{-2}	0.32

hence, to a photocurrent. Also, light acceptor or donor doping of the polymers should lead to a system of IR active, paramagnetic, *dopant-pinned* polarons. At a higher dopant concentration this system could exhibit a transition to a diamagnetic bipolaron lattice or liquid.

Recent experimental studies[17,20] of hole mobility in the polysilylenes suggest that transport in the polysilylenes involves hopping among states associated directly with the silicon backbone rather than the pendant sidegroups and that these states are not fully extended over the polymer but remain relatively localized. This is consistent with the present theoretical results. The significant point for transport is that interchain hopping of the hole—which presumably is the rate limiting process—proceeds through the self generated intragap states and *simulates* hopping among molecular sites.[21]

We are currently extending (1) to include the effects of the side groups R and hence, of full ground-state band structures for particular group IVA homopolymers.

Acknowledgments

We thank R. Bigelow, D. J. Chadi, G. E. Johnson, C. Mailhiot, M. Stutzmann and M. Stolka for valuable discussion of this work and R. G. Kepler for stimulating correspondence.

References

1. M. J. Rice, *Phys. Lett.*, **71A**, 152 (1978); W. P. Su, J. R. Schrieffer and A. J. Heeger, *Phys. Rev. Lett.*, **42**, 1698 (1979) and *Phys. Rev.*, **B22**, 2099 (1980).
2. See e.g., A. J. Heeger in *Handbook of Conducting Polymers*, Ed. T. A. Skotheim (Marcel Dekker, Inc., New York, 1986) Volume 2, pp. 729–756.
3. An initial account of this work has been given by M. J. Rice and S. R. Phillpot, *Phys. Rev. Lett.*, **58**, 937 (1987); M. J. Rice, S. R. Phillpot and S. Jeyadev (to be published).
4. R. West, *J. Organometall. Chem.*, **300**, 327 (1986); G. Loubriel and J. Zeigler, *Phys. Rev.*, **B33**, 4203 (1986).
5. P. Trefonas and R. West, *J. Polymer Science: Poly. Chem. Ed.*, **23**, 2099 (1985).
6. S. A. Brazovski and N. N. Kirova, *JETP Lett.*, **33**, 4 (1981) [English trans. of *Pis ma Zh. Eksp. Teor, Fiz.*, **33**, 6 (1981)]. A. R. Bishop and D. K. Campbell in *Nonlinear Problems: Present and Future*, Eds. A. R. Bishop et al. (North Holland, Amsterdam, 1982) p. 195.
7. For an excellent review, see R. R. Chance et al. in *Handbook of Conducting Polymers*, Ed. T. A. Skotheim (Marcel Dekker, Inc., New York, 1986) Volume 2, pp. 825–857.
8. P. Trefonas III, R. West, R. D. Miller and D. Hofer, *J. Polymer Sci: Poly. Lett. Ed.*, **21**, 823 (1983) and references therein.
9. W. A. Harrison, *Electronic Structure and the Properties of Solids* (The Physics of the Chemical Bond) (W. H. Freeman and Co., San Francisco, 1979) Chapter 2.

10. D. J. Chadi, *Phys. Rev. Lett.*, **41**, 1062 (1978).
11. Compare G. Leman and J. Friedel, *J. Applied Physics* (Supplement) **33**, 281 (1962). These authors consider a diamond crystal structure for which there are not two but four nearest neighbour interactions. Consequently, they find $E_g = 2V - 4\Delta$ rather than $E_g = 2V - 2\Delta$.
12. V. I. Melnikov, *Sov. Phys. JETP*, **45**, 1233 (1977) [English Trans. of *Zh. Eksp. Teor. Fiz.*, **72**, 2345 (1977)). P. B. Shaw and G. Whitfield, *Phys. Rev.*, **B17**, 1495 (1978). L. A. Turkevich and T. D. Holstein, *Phys. Rev.*, **B35**, 7474 (1987).
13. M. Kumada and K. Tamao, *Adv. Organometal Chem.*, **6**, 80 (1968); W. G. Boberski and A. L. Allred, *J. Organometal Chem.*, **71**, C27 (1974).
14. C. G. Pitt, R. N. Carey and E. C. Toren Jr., *J. Am. Chem. Soc.*, **94**, 3806 (1972); K. Takeda, N. Matsumoto and M. Fukuchi, *Phys. Rev.*, **B30**, 5871 (1984); R. W. Bigelow, *Organometallics*, **5**, 1502 (1986).
15. W. B. Pollard and G. Lucovsky, *Phys. Rev.*, **B26**, 3172 (1982).
16. M. Stolka, H.-J. Yuh, K. McGrane and D. M. Pai, *J. Polymer Sci.: Poly. Chem. Ed.*, **25**, 823 (1987).
17. R. G. Kepler, J. M. Zeigler, L. A. Harrah and S. R. Kurtz, *Phys. Rev.*, **B35**, 2818 (1987).
18. L. A. Harrah and J. M. Zeigler, *Polymer Preprints*, **27**, (2), 356 (1986); G. E. Johnson, *Polymer Preprints*, **27**, (2), 352 (1986).
19. We find $B/r_o^l = 2.07$ eV and $l = 6.22$.
20. M. Abkowitz, F. E. Knier, H.-J Yuh, R. J. Weagley and M. Stolka, *Solid State Commun.*, **62**, 547 (1987); M. A. Abkowitz and M. Stolka, *Proc. of the IUPAC International Symposium on Polymers for Advanced Technologies*, Jerusalem, 1987 (VCH Publishers, New York), to be published.
21. H. Bässler, G. Schönherr, M. Abkowitz and D. M. Pai, *Phys. Rev.*, **B26**, 3105 (1982).